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NO$_x$ Reduction Methods and Apparatuses

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PATENT RIGHTS STATEMENT

[0001] This invention was made with Government support under Contract DE/AC0676RLO1830 awarded by the U.S. Department of Energy. The Government has certain rights in the invention.

TECHNICAL FIELD

[0002] The invention pertains to methods of reducing NO$_x$ and apparatuses for reducing NO$_x$.

BACKGROUND OF THE INVENTION

[0003] A wide variety of technology exists that is aimed at reducing NO$_x$, wherein x is greater than zero, in emission sources. As emission limits decrease and cost reductions are desired, new NO$_x$ emission control methods are being evaluated. One emission source identified for improved NO$_x$ reduction includes lean burn spark and compression ignition engine exhaust. One example of such an emission source includes diesel engines.

[0004] A desire exists to improve NO$_x$ reduction for emission sources including, but not limited to, diesel engines.

SUMMARY OF THE INVENTION

[0005] In one aspect of the invention, a NO$_x$ reduction method includes treating a first gas containing NO$_x$, wherein x is greater than zero, and producing a second gas containing NO$_2$. A portion of the NO$_2$ in the second gas can be

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reduced to N_2 and a third gas produced containing less NO_x than the first gas, substantially all of the third gas NO_x being NO. The third gas can be treated and a fourth gas produced containing NO_2. A portion of the NO_2 in the fourth gas can be reduced to N_2 and a fifth gas produced containing less NO_x than the third gas, substantially all of the fifth gas NO_x being NO. As one example, a fraction of the first gas NO_x treated to second gas NO_2 can approximately equal a fraction of the third gas NO_x treated to fourth gas NO_2. Also, the portion of the second gas NO_2 reduced can be less than about 70 volume percent (vol%).

[0006] In another aspect of the invention, a NO_x reduction method includes treating a first gas containing NO_x, wherein x is greater than zero, with a first plasma and producing a second gas containing NO_2. The method includes reducing a portion of the NO_2 in the second gas to N_2 with a first catalyst and producing a third gas containing less NO_x than the first gas, substantially all of the third gas NO_x being NO. The third gas containing NO_x can be treated with a second plasma and a fourth gas produced containing NO_2. A portion of the NO_2 in the fourth gas can be reduced to N_2 with a second catalyst and a fifth gas produced containing less NO_x than the third gas. As an example, the first and third gases can further contain hydrocarbon. Treating the first gas and reducing a portion of the NO_2 in the second gas can provide oxidation of less than 50 vol% of the hydrocarbon in the first gas. Treating the third gas and reducing a portion of the NO_2 in the fourth gas can provide oxidation of less than 50 vol% of the hydrocarbon in the third gas. The method can further include controlling energy consumption of the first and second plasmas independent of each other. A combined energy consumption of the first and second plasmas can be substantially minimized.

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[0007] In yet another aspect of the invention, a NO_x reduction method can include performing a step at least three times in series. The step includes converting NO_x, wherein x is greater than zero, comprised by an inlet gas to NO_2 with a plasma and catalytically reducing NO_2 at least to N_2 and NO comprised by an outlet gas. The at least three performances of the step can be operated to plasma convert approximately equal fractions of the inlet gas NO_x to NO_2. As an example, the outlet gas of at least two of the three performances of the step can comprise the inlet gas for a subsequent performance of the step.

[0008] In a further aspect of the invention, a NO_x reduction apparatus includes a plurality of reactor units in series. Individual reactor units include a plasma device and a reducing catalyst. The plasma device exhibits the property of converting NO_x, wherein x is greater than zero, to NO_2. The reducing catalyst exhibits the property of reducing NO_2 to a reaction product consisting essentially of N_2 and NO. The apparatus can further include a plurality of separate power control devices for respective plasma devices of individual reactor units. The plasma devices can include dual dielectric barrier discharge devices. The reducing catalysts can include at least one of barium zeolite Y type (Ba-Y) and sodium zeolite Y type (Na-Y).

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Preferred embodiments of the invention are described below with reference to the following accompanying drawings.

[0010] Fig. 1 is a flow diagram showing a NO_x reducing method according to one aspect of the invention.

[0011]   Fig. 2 is a line chart showing energy consumption at various extents of reaction (ε) for some initial concentrations of NO.

[0012]   Fig. 3 is a line chart showing the extent of reaction (ε) at various numbers of steps (S) using a catalyst efficiency of 60% to meet 90% NO_x reduction.

[0013]   Fig. 4 is a line chart showing the effect of different catalyst efficiencies on energy consumption in comparison the number of steps (S).

[0014]   Fig. 5 is a line chart showing energy consumption at various initial concentrations of NO for some catalyst efficiencies, assuming five steps.

[0015]   Fig. 6 is a line chart showing energy consumption at various initial concentrations of NO for a system set to reduce NO to 7 ppm or by 90 volume percent (vol%), whichever is greater.

[0016]   Fig. 7 is a line chart showing energy consumption at various voltages for a first tube array reactor, a second tube array reactor, and the two tube array reactors combined.

[0017]   Fig. 8 is a line chart showing the vol% of NO reduced at various levels of energy usage for a one reactor and two reactor apparatus.

[0018]   Fig. 9 is a line chart showing the vol% of NO reduced at various levels of energy consumption for a one reactor apparatus and some energy inputs to a second reactor of a two reactor apparatus.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019]   A variety of investigations have occurred regarding plasma assisted catalytic treatment of NO_x, wherein x is greater than zero, in lean burn automobile and light duty diesel exhaust. Normally, x is also 3 or less, but the

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majority of NO_x frequently exists as NO. Thus, studies often use synthetic exhaust containing only NO as the NO_x to approximate practical conditions. One example of plasma assisted catalytic treatment of NO_x includes using plasma discharge to convert NO_x to NO_2 and providing a catalyst to convert NO_2 to N_2. The various aspects of the invention described herein may have special utility with regard to lean burn spark and compression ignition engine exhaust, but are also applicable to reducing NO_x from other sources, as readily understood by those of ordinary skill in the art. Prior investigations have experienced difficulty in obtaining a 90 volume percent (vol%) NO_x conversion. Effective catalysts previously tested have exhibited an upper limit less than 90 vol% under ordinary exhaust conditions.

[0020] Further investigation has newly revealed that the most efficient current catalysts release unconverted NO_x in the form of NO even when enough energy is input through plasma treatment to ensure that all NO_x reaches the catalyst as NO_2. Observation further indicates that most of the hydrocarbon input survives both the plasma and the catalyst. As a result, a composition output from plasma assisted catalytic treatment of this type can be very similar to an input composition prior to the treatment, although with lower overall NO_x and hydrocarbon concentrations. A conventional approach to resolving the difficulties mentioned could include applying more plasma energy and/or a larger volume catalyst bed. However, findings indicate that a second application of plasma followed by a second catalyst bed can improve overall plasma-catalyst reactor performance. The improvement includes both increasing the level of NO_x conversion as well as reducing plasma energy consumption for a given level of NO_x reduction.

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[0021] Although the observations described herein were ascertained in the context of plasma assisted catalytic NO_x treatment, the principles described herein can be applied to other NO_x reduction methods. Accordingly, in one aspect of the invention, a NO_x reduction method includes treating a first gas containing NO_x, wherein x is greater than zero, and producing a second gas containing NO_2. For the most part, the treating NO_x and producing NO_2 includes oxidation of NO_x, wherein x is greater than zero and less than 2. However, reduction of NO_x compounds, wherein x is greater than 2 could also occur depending on the composition of the first gas. The method further includes reducing a portion of the NO_2 in the second gas to N_2 and producing a third gas containing less NO_x than the first gas, substantially all of the third gas NO_x being NO. The method also includes treating the third gas, producing a fourth gas containing NO_2, reducing a portion of the NO_2 in the fourth gas to N_2, and producing a fifth gas containing less NO_x than the third gas, substantially all of the fifth gas NO_x being NO. The treating of the first gas and/or the third gas and producing the second and/or fourth gas containing NO_2 can include treating with a plasma, as well as perhaps various oxidation techniques. Substantially all of the first gas NO_x can be converted to NO_2 comprised by the second gas. Also, the reducing of a portion of the NO_2 in the second and/or fourth gas to N_2 can include reducing the NO_2 with a catalyst.

[0022] A variety of options and variations exist for the above described methods. For example, the treating of the first gas can occur separately from the reducing of NO_2 in the second gas and the treating of the third gas can occur separately from the reducing of NO_2 in the fourth gas. In a two-stage reactor configuration, a first stage of the reactor can provide a plasma or oxidation

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region where treating of the first gas can occur. A second stage of the reactor can provide a catalyst or reducing region where reducing a portion of the NO_2 in the second gas can occur.

[0023] Alternatively, the treating and reducing can occur together, as in a single-stage reactor configuration where catalyst is provided within a plasma or oxidation region. Thus, treating a first gas and reducing a portion of a second gas occur together rather than separately in different stages of a reactor. When NO_2 remains after the single-stage, then an additional catalyst stage could be provided to further reduce NO_2. As one example, a continuous catalyst bed could be used with a plurality of distributed plasma or oxidation regions along the continuous catalyst bed. Catalyst-only or reducing regions could also be used along the continuous catalyst bed downstream of the plasma or oxidation regions. The method thus could include use of a single-stage reactor configuration in regions where plasma and catalyst are combined and use of a two-stage reactor configuration by providing additional catalyst-only or reducing regions. Other methods are also conceivable using different combinations of the two-stage and/or single-stage concepts described herein.

[0024] The first and third gases can further include hydrocarbon. The treating of the first gas and reducing a portion of the NO_2 in the second gas can provide oxidation to CO_2/CO and H_2O of less than 50 vol% of the hydrocarbon in the first gas. The treating of the third gas and reducing a portion of the NO_2 in the fourth gas can provide oxidation to CO_2/CO and H_2O of less than 50 vol% of the hydrocarbon in the third gas. The method can include oxidizing less than 35 vol% of the hydrocarbon in the first and third gases. The portion of the second

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gas NO_2 reduced can be less than about 70 vol%. For example, the portion of second gas NO_2 reduced can be from about 50 vol% to about 60 vol%.

[0025] Despite the relatively low amount of second gas NO_2 reduction, the aspects of the invention described herein can provide for attaining at least 90% reduction to N_2 of the first gas NO_x. In circumstances where a catalyst exhibits less than 90 vol% reduction of NO_2 to N_2, the described methods nevertheless allow obtaining at least 90 vol% NO_x reduction. As indicated, the described methods may also apply to non-catalytic techniques for reducing NO_2 to N_2.

[0026] The portion of the second gas and/or fourth gas NO_2 not reduced to N_2 is comprised by the third and fifth gases, respectively, as NO_x. Preferably, substantially all of the third and/or fifth gas NO_x exists as NO. While "substantially all" indicates a high percentage of the NO_x as NO, it can be less than 100 vol% allowing for small amounts of other NO_x compounds. Alternatively, all of the third and/or fifth gas NO_x can be NO.

[0027] One explanation for the presence of NO in the third gas is that the portion of the NO_2 not reduced to N_2 reverts to NO. Some reducing catalysts exhibit such a property, for example, barium zeolite Y type, sodium zeolite Y type, and potentially others. The first gas can include hydrocarbon that forms partially oxidized hydrocarbons, such as acetaldehyde, propionaldehyde, etc. during treating. Such partially oxidized hydrocarbons can act as reducing agents during the reducing of a portion of the second gas NO_2. Accordingly, the third gas can include a majority of the hydrocarbon existing in the first gas. A composition of the third gas including NO and hydrocarbon provides an opportunity for successively treating the gas to produce NO_2 and reducing a portion of the NO_2 to produce a gas comprising less NO_x. Accordingly, the

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method described above can further include treating the fifth gas and producing a sixth gas containing NO_2. A portion of the NO_2 in the sixth gas can be reduced to N_2 and a seventh gas produced containing less NO_x than the fifth gas, substantially all of the seventh gas NO_x being NO.

[0028]   According to another aspect of the invention, a NO_x reduction method includes treating a first gas containing NO_x, wherein x is greater than zero, with a first plasma and producing a second gas containing NO_2. The method provides reducing a portion of the NO_2 in the second gas to N_2 with a first catalyst and producing a third gas containing less NO_x than the first gas, substantially all of the third gas NO_x being NO. The third gas containing NO_x can be treated with a second plasma and a fourth gas produced containing NO_2. A portion of the NO_2 in the fourth gas can be reduced to N_2 with a second catalyst and a fifth gas produced containing less NO_x than the third gas. As an option, substantially all of the fifth gas NO_x can be NO. Such a composition will likely result in a circumstance where the first catalyst exhibits a composition the same as the second catalyst, although other processing techniques may produce the composition. The method can further include treating the fifth gas with a third plasma, producing a sixth gas containing NO_2, reducing a portion of the NO_2 in the sixth gas to N_2 with a third catalyst, and producing a seventh gas containing less NO_x than the fifth gas.

[0029]   In a further aspect of the invention, a NO_x reduction method can include performing a step at least three times in series, the step can include converting NO_x, wherein x is greater than zero, comprised by an inlet gas to NO_2 with a plasma and catalytically reducing NO_2 at least to N_2 and NO comprised by an outlet gas. The method includes operating the at least three performances of

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the step to plasma convert approximately equal fractions of the inlet gas NO_x to NO_2. As examples, the outlet gas of at least two of the three performances of the step can comprise the inlet gas for a subsequent performance of the step. Also, similar to earlier descriptions, the step can further include oxidizing hydrocarbon from the inlet gas, the outlet gas containing greater than 50 vol% of the hydrocarbon from the inlet gas. The at least three performances of the step can be substantially identical. The at least three performance can also be performed differently and yet convert approximately equal fractions of the inlet gas NO_x to NO_2.

[0030] Fig. 1 shows a flow diagram of a NO_x reduction method encompassed by the aspects of the invention described herein. In a first step, an engine source of NO_x contains an initial concentration of NO comprised by an inlet gas to a discharge plasma. The discharge plasma consumes an amount of energy E_1 and exhibits an extent of reaction, ε, in the discharge plasma defined as 1-($[NO]_{OUT}/[NO]_{IN}$). The discharge plasma produces some generally unknown but very reactive species called "X" at some rate k_P proportional to the applied power per unit volume of inlet gas. This material is lost by quenching at some rate k_Q and by reaction with NO at a rate k_R to eventually yield NO_2.

[0031] X is believed to be produced locally and continuously in the discharge plasma and presumably very little is carried downstream. Accordingly, a steady state approximation can be made that the concentration of X does not change with respect to time. Differential equations written for the concentration of X and NO can be solved to produce Equation 1 giving energy density, Ev, as a function of extent of reaction and initial NO concentration as follows:

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$$Ev = \beta_0 \ln\left(\frac{1}{1-\varepsilon}\right) + \frac{1}{k_P}\varepsilon[NO]_{IN} \qquad (1)$$

wherein β_0 is defined as $k_Q/k_R k_P$ and ε is defined as above. A typical measured value of β_0 can equal 3 Joule/Liter (J/L) and k_P can equal 9 ppm-L/J using the unfiltered exhaust stream of a diesel generator. Such typical values are presented here for illustrative purposes since the actual values depend on a variety of factors including design of the reactor containing the discharge plasma, temperature, gas composition (such as oxygen, water, and hydrocarbon concentration), and the extent of soot accumulation. Figure 2 shows a line chart of energy density at various extents of reaction for five initial concentrations of NO. Understandably, as the extent of converting NO to NO_2 increases and the initial concentration of NO increases, energy consumption also increases.

[0032] Observation indicates that under lean burn conditions in a lean burn spark and compression ignition engine exhaust the oxygen content typically does not fall below the amount desired for efficient conversion of NO to NO_2. Excess oxygen or water tends to reduce the efficiency of NO oxidation primarily because of negative ions formed. Hydrocarbons tend to suppress reaction of radicals with NO_2 that convert it back to NO. Also, as indicated, partially oxidized hydrocarbons can improve the efficiency of subsequent catalyst reduction steps. Accordingly, the discharge plasma can provide further benefits aside from merely oxidizing NO to NO_2. Some investigation has indicated that certain small hydrocarbons such as methane, ethane, ethene, and acetylene, as well as highly unsaturated hydrocarbons such as benzene and polyaromatic hydrocarbons, might not be effective in suppressing reaction of radicals with NO_2 and improving the efficiency of catalytic reduction.

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[0033] One example of a suitable discharge plasma includes a dual dielectric barrier discharge device, as known to those skilled in the art. Other plasma devices can be provided in the alternative. In a dual dielectric barrier discharge device, power is delivered to the gas comprising NO_x using micro discharges. The micro discharges typically occur from about 10 to about 100 nanoseconds in length and are highly localized within the device. Preferably, the micro discharges tend to fill the device volume and produce a uniform blue glow in air at 1 atmosphere.

[0034] Gas flowing from the discharge plasma shown in Fig. 1 enters a catalyst stage exhibiting an efficiency of χ_{CAT} for reducing NO_2 to N_2 and perhaps non-NO_x byproducts including N_2O, HCN, etc. Although technically within the NO_x definition used herein, N_2O is not included as NO_x in measuring χ_{CAT} since it is not currently regulated as NO_x in the United States of America. In the event of regulatory changes, N_2O could easily be included in measuring χ_{CAT}. A concentration of NO indicated in Fig. 1 as $[NO]_1$ exits the first step of the NO_x reduction method and proceeds to a second step. Some number of steps, S, each including a discharge plasma stage and a catalyst stage can be used to obtain a desired level of NO_x reduction. Notably, Fig. 1 assumes an extent of reaction for the discharge plasma and a catalyst efficiency substantially equivalent in each step. However, different discharge plasmas and/or catalysts or catalyst bed designs could be used in the various steps creating different extents of reaction and catalyst efficiencies in the steps.

[0035] Fig. 3 shows a line chart of the extent of reaction at various numbers of steps that will meet a target of 90 vol% NO_x reduction assuming a catalyst efficiency of 60%. Fig. 1 assumes an adequate hydrocarbon concentration and

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catalyst volume to convert all NO_2 from each discharge plasma to N_2 or NO. Accordingly, no NO_2 enters the plasma discharge of a subsequent step. The minimum S is given by Target $\geq (1\text{-}\chi_{CAT})^S$, where Target is defined as $[NO_x]_{exhaust}/[NO_x]_{engine}$. Algebraic manipulation yields Equation 2 as follows:

$$\varepsilon = \frac{1 - T \arg et^{1/S}}{\chi_{CAT}} \qquad (2)$$

used to produce Fig. 3. In Fig. 3, a three step reduction method could obtain the 90 vol% NO_x reduction by oxidizing at least 90 vol% of the NO to NO_2 in the plasma discharge at each step. For a fifteen step method, as little as 25 vol% of the NO could be oxidized at each step and still meet the 90 vol% NO_x reduction target.

[0036]   Further algebraic manipulation can be used to produce an expression for total electrical energy as follows in Equation 3:

$$Ev_{Total} = \beta_0 S \ln\left(\frac{1}{1-\varepsilon}\right) + \frac{1 - T \arg et}{\chi_{CAT}} \frac{[NO_x]_{exhaust}}{k_P} \qquad (3)$$

which is used to generate Fig. 4. Fig. 4 assumes that β_0 is 3, k_P is 9, $[NO]_{engine}$ is 75 ppm and Target is 0.10 (NO_x reduction of 90 vol%). Fig. 4 shows that increasing χ_{CAT} reduces energy consumption. Fig 4 also shows that as χ_{CAT} decreases the significance of providing multiple steps increases as a way to reduce energy consumption. For example, in the limiting case where χ_{CAT} is 1, no advantage exists regarding energy consumption in providing multiple steps. When χ_{CAT} is 0.9, the reduction in energy consumption appears less significant for providing multiple steps in comparison to when χ_{CAT} is 0.6. Equation 3 can also be used to generate Fig. 5 by choosing S as 5 and varying $[NO]_{engine}$. Fig. 5

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shows that energy consumption increases with increasing initial NO_x concentration in an essentially linear fashion.

[0037] The mathematical manipulations to obtain Equation 3 above included finding the energy at each step. It was determined that total energy consumption can be minimized by making ε identical at each step. Accordingly, Equation 4 can be written for the energy of a given step k as follows:

$$Ev_k = \beta_0 \ln\left(\frac{1}{1-\varepsilon}\right) + \varepsilon(2\varepsilon - \varepsilon\chi_{CAT} - 1)^{k-1} \frac{[NO_x]_{exhaust}}{k_P} \qquad (4)$$

and used to establish that energy consumption decreases for each step of the method. The methods described above can further include controlling energy consumption in the first and second plasmas independent of each other such that the discharge plasmas exhibit substantially the same ε. Fig. 2 shows that for a given ε the energy consumption of a step will decrease as the initial NO_x concentration decreases. Accordingly, such a control scenario provides one example of how combined energy consumption of the first and second plasmas can be substantially minimized. Where additional steps are used in a NO_x reduction method, minimization of total energy usage for plasma conversion of NO_x to NO_2 can be accomplished similarly for some or all of the performances of the steps. In keeping with the principles described herein regarding energy consumption, additional opportunities can be identified for minimizing energy in the various aspects of the invention.

[0038] Understandably, a circumstance may exist where instead of a percentage of inlet NO_x reduced as a target, a target could be a numerical concentration of NO_x. The equations described above and various aspects of the invention also apply to a numerical concentration target. For example, Fig. 6

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shows a line chart of energy consumption at various values of NO concentration using both a 90 vol% target and a 7 ppm NO_x target. That is, the hypothetical system described by Fig. 6 is set to reduce NO_x to 7 ppm or by 90 vol%, whichever is greater. When NO_x falls below 7 ppm, treatment ceases.

[0039]   In keeping with various aspects of a NO_x reduction method above, the invention also includes various NO_x reduction apparatuses. According to one aspect of the invention, a NO_x reduction apparatus includes a plurality of reactor units in series, individual reactor units including a plasma device and a reducing catalyst. The plasma device can exhibit the property of converting NO_x, wherein x is greater than zero, to NO_2. The reducing catalyst can exhibit the property of reducing NO_2 to a reaction product consisting essentially of N_2 and NO. Various catalyst efficiencies are represented herein for reducing NO_2 to N_2. NO_2 reduced to N_2 can be less than about 70 vol%. The NO_2 reduced can also be from about 50 vol% to about 60 vol%. Largely, the portion of the NO_2 not reduced to N_2 is converted to NO such that the reaction product consists essentially of N_2 and NO. The reaction product can include trace amounts of other chemical species, such as N_2O, HCN, etc. and still consist essentially of N_2 and NO. However, the reaction product can instead consist of N_2 and NO.

[0040]   The plasma device and reducing catalyst of the NO_x reduction apparatus can be separated. Also, at least one of the plurality of reactor units can exhibit the property of oxidizing less than 50 vol% of hydrocarbon input to CO/CO_2 and H_2O. The at least one reactor unit can oxidize less than 35 vol% of the hydrocarbon input. The reactor units' catalysts can exhibit a same composition. Preferably, the reducing catalysts include at least one of barium zeolite Y type and sodium zeolite Y type. The plasma devices can include dual

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dielectric barrier discharge devices. Further, the plurality of reactor units can include three reactor units. The NO_x reduction apparatus can further comprise a plurality of separate power control devices for respective plasma devices of individual reactor units. Separate power control devices provide the advantage of controlling the energy consumption of the plasma devices independently. Accordingly, independent power control provides for substantially minimizing combined energy consumption of the plasma devices by plasma converting the same amount of NO_x to NO_2 in individual plasma devices of the reactor units.

[0041] The plurality of reactor units in series can also be referred to as a cascaded reactor system. Such a system can be engineered with a robust design. As one example, providing more reactor units than sufficient to reach a target NO_x reduction allows the advantage that loss of a single reactor unit imposes little impact on the performance and/or energy requirements for the NO_x reduction apparatus. In such circumstance, increase in energy supply to remaining reactor units compensates for the loss of a single reactor unit. More redundant reactor units can be provided for an even more robust design. As can be seen from Equation 4, the addition of redundant reactor units reduces the extent of reaction of each unit and correspondingly reduces the power consumption of each unit. Reducing power and voltage applied to the plasma devices extends the life of the plasma devices, a power supply to the devices, and the associated electrical connections. Further, providing redundant reactor units might even justify sizing reactor units and the associated power supplies smaller than otherwise warranted.

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Example

[0042] An apparatus was configured including separate plasma discharge and catalyst stages that were separately heated. The plasma discharge was generated in a double dielectric barrier device called a tube array reactor (TAR). The TAR plasma was generated between an array of oppositely polarized electrodes inside single ended alumina tubes suspended in a synthetic gas stream to be oxidized. The distance between oppositely polarized tubes can be maintained between 1 and 3 millimeters (mm). A larger separation of electrodes could be used as a way to reduce back pressure, but might produce significantly higher turn-on voltage. For the present example, 2 mm electrode spacings were used. A large TAR had three high voltage electrodes surrounded by a grid of eight ground electrodes. A small TAR had two high voltage electrodes surrounded by six ground electrodes. Both TARs were machined from high temperature machinable ceramic material and the alumina tubes were held in place by high temperature RTV adhesive. Locating the outermost ground electrodes against the reactor walls allowed all of the gas flow through the discharge regions. The large TAR was used as the first plasma stage and the small TAR was used as the second plasma stage. Both TARs were operated with sinusoidal high voltage at 400 hertz from high voltage transformers.

[0043] The catalyst stages were configured using barium zeolite Y type catalyst formed from sodium zeolite Y type catalyst (CBV-100) obtained in extrudate form from Zeolyst International (Valley Forge, Pennsylvania) and ion exchanged with barium. The space velocity for each bed was operated at 12,000 per hour. Accordingly, each bed held 10 cubic centimeters of extrudate to provide the desired space velocity for a 2 standard liter per minute (slm) flow.

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The overall hourly space velocity was therefore 6,000 per hour. A synthetic exhaust mixture was used containing 2 vol% water, 6 vol% oxygen, 200 ppm NO, and 600 ppm propene with the balance N_2. Water was added at room temperature by diverting the nitrogen plus oxygen flow through a water bubbler, limiting water concentration to about 2 vol% but enabling operation without heated lines. The TARs were maintained at 100 C and the catalyst stages were maintained between 160 and 180 C.

[0044] NO_x data was obtained using either a chemiluminescent analyzer (CLA) (California Analytical Model 400-HCLD) or a Fourier Transform Infrared Spectrometer (FTIR) (Nicolet Magna-IR560) equipped with a 2 meter gas cell and operated at 0.5 centimeter^{-1} resolution. Pressure was controlled at 760 Torr and temperature at 165 C.

[0045] Fig. 7 shows calibration measurements for energy deposited into plasmas of the first and/or second TARs at various voltages. Fig. 8 illustrates the vol% of NO_x reduced in the test apparatus using only the first TAR and both TARs in combination. At low power little difference exists in the vol% reduction for one TAR compared to two TARs. However, the energy savings possible by using a second TAR is exemplified by observing the relative energy consumption at 70 vol% NO_x conversion. Operating with one TAR requires noticeably more energy in comparison to operating with two TARs to achieve 70 vol%. Further, for the nominal energy consumption target of 15 J/L a significantly higher vol% conversion can be obtained using two TARs in comparison to one TAR.

[0046] Fig. 9 shows vol% NO_x conversion data taken using independent control of power to the first and second TAR. One line is shown representing supplying power only to the first TAR. Four additional lines are shown wherein

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the power to the first TAR was fixed at the beginning point of each of such curves and the power to the second TAR increased to establish a higher vol% NO_x reduction. Notably, the highest vol% NO_x reduction was obtained by supplying about 15 J/L to the first TAR and supplying an almost equivalent additional amount of energy to the second TAR. Although a target of at least 90 vol% reduction was not obtained, it seems apparent that adding a third reactor unit may enable attaining higher vol% reduction. Fig. 9 also exemplifies the potential energy savings available using separate energy controls for the TARs. In Fig. 9, 80 vol% NO_x reduction was attained at about 14.4 J/L with about 8.4 J/L supplied to the first TAR and the remaining 6 J/L supplied to the second TAR. The data in Fig. 8 was generated using equal energy supply to each TAR and consumed about 18J/L total energy to attain 80 vol% NO_x reduction. Accordingly, an energy savings of about 20% was realized by providing independent control of energy consumption to the first and second TARs.

[0047] In compliance with the statute, the invention has been described in language more or less specific as to structural and methodical features. It is to be understood, however, that the invention is not limited to the specific features shown and described, since the means herein disclosed comprise preferred forms of putting the invention into effect. The invention is, therefore, claimed in any of its forms or modifications within the proper scope of the appended claims appropriately interpreted in accordance with the doctrine of equivalents.